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Monoaromatic compounds in ambient air of various cities: a focus on correlations between the xylenes and ethylbenzene

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Abstract

Speciation of *o*-xylene, *m*-xylene, *p*-xylene and ethylbenzene was performed by gas chromatography from ambient air and liquid fuel samples collected at various locations in 19 cities in Europe, Asia and South America. The xylene's mixing ratios were compared to each other from the various locations, which included urban air, traffic air and liquid fuel. For all samples, the xylenes exhibited robust correlations, and the slopes remained constant. The *m*-xylene/*p*-xylene ratio was found to be 2.33 ± 0.30, and the *m*-xylene/*o*-xylene ratio was found to be 1.84 ± 0.25. These ratios remain persistent even in biomass combustion experiments (in South America and South Africa). Comparing the xylenes to toluene and benzene indicate that combustion, but not fuel evaporation, is the major common source of the xylenes in areas dominated by automotive emissions. Although a wide range of combustion types and combustion efficiencies were encountered throughout all the locations investigated, xylenes and ethylbenzene ratios remained persistent. We discuss the implications of the constancies in the xylenes and ethylbenzene ratios on atmospheric chemistry.

Keywords: Gas chromatography; *m*-xylene and *p*-xylene speciation; Alkylbenzenes; Tropospheric air; Urban plume

1. Introduction

Hydrocarbons are significant components in urban air because of combustion, solvent and fuel evaporation and tank leakage. Among them, most of the aromatic compounds are listed as toxic air contaminants (e.g. benzene) or *potential* toxic air contaminants (e.g. toluene, xylenes) (Hanson, 1996). During daytime hours, once released into the atmosphere, aromatic components undergo OH oxidation, and thus participate in the formation of urban and suburban photochemical smog. The total ozone attributable to each organic compound is influenced greatly by the relative concentration of each species. Based on 1987 non methane hydrocarbon emissions in the United Kingdom, Derwent and Jenkin (1991) calculated that *m*-xylene, trimethylbenzenes and C_3–C_5 alkenes produce as much or more ozone than ethylene. Furthermore, the reaction products from the atmospheric oxidation of individual alkylbenzenes include potential toxic and mutagenic compounds such as aromatic aldehydes, quinones, dicarbonyls, epoxides (Kwok et al., 1997; Yu and Jeffries, 1997; Yu et al., 1997; Kleindienst et al., 1999) and secondary organic aerosols (Odum et al., 1997; Kourtidis and Ziomas, 1999; Kleindienst et al., 1999).

Because of the potential hazards associated with the alkylbenzenes, it is important to accurately determine the atmospheric mixing ratios of these gases and to identify their main sources. Although a large number of studies

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have investigated these issues, only a few of the laboratories making the measurements were able to resolve the three xylenes and ethylbenzene (Wathne, 1983; Zweidinger et al., 1988; Olson et al., 1992; Tsujino and Kuwata, 1993; Rappenglück et al., 1998). However, each of the above-mentioned study investigated one particular site at a time, and the number of samples was limited. All the other studies reported the sum of *m*- and *p*-xylene mixing ratios. Because of the lack of speciated xylene data, in calculating the photochemical ozone creating potential (POCP) and photochemical PAN creating potential (PPCP) values, Derwent and Jenkin (1991) and Derwent (1995) assumed that *m*- and *p*-xylene were equally present in the atmosphere in the UK.

The current study presents hydrocarbon speciation including clean separation of the xylenes and ethylbenzene by multi-column gas chromatography. The purpose is to determine the concentrations of *m*- and *p*-xylene and other alkylbenzenes concentration ratios in a large number of samples taken at various locations throughout the world. This allows us to confirm and improve the method proposed by Nelson and Quigley (1983) to determine the extent of photochemical reactivity in ambient air by measuring the ratios between $(m+p)$-xylene (taken together) and ethylbenzene. The final purpose is the identification of the main source of these gases.

2. Experimental section

2.1. Sampling

Air samples were collected in 2-l electropolished stainless-steel canisters. Nineteen cities in Europe, Asia and South America were investigated at various times of the year in 1994, 1996, 1997 and 1998 (Table 1). "Urban air" samples were collected throughout each city, in parks and aerated areas, far removed from roadways or any known local source influence. The collections were performed within the city limits, not in the suburbs. "Traffic air" samples were collected on roadways or in motorway tunnels with fluid traffic. A relatively long sampling period was used for the traffic samples in order to damp out any influence of one particular car passing the sampling site. Each sampling period was integrated over several minutes.

2.2. Sample analysis

The whole air samples collected during the city studies were analyzed for NMHCs, halocarbons and alkyl nitrates using a four gas chromatograph (GC), six column, six detector system. A 250 ml (STP) aliquot from each canister was trapped on a glass bead filled $\frac{1}{4}$-inch

Table 1
Cities studied – number of samples collected in the present study

City	Country	Date	Urban air	Traffic air	Liquid fuel		
					Unleaded	Leaded	Diesel
Berlin	Germany	Oct/Nov 1994	27	4	—	—	—
Buenos Aires	Brazil	Nov 1996	1	—	—	—	—
Bangkok	Thailand	May 1997	—	—	1	1	1
Bucharest	Romania	Oct/Nov 1994	15	1	—	—	—
Budapest	Hungary	Oct/Nov 1994	17	—	—	—	—
Dresden	Germany	Oct/Nov 1994	16	—	—	—	—
Hong-Kong	China	May 1997	—	—	1	1	1
Hong-Kong	China	Dec 1997	32		—	—	—
Krakow	Poland	Oct/Nov 1994	15	1	—	—	—
London	UK	Oct/Nov 1994	14	1	—	—	—
Paris	France	June 1996	48		—	—	—
Paris	France	June 1998	—	3	2	1	1
Paris	France	Oct/Nov 1994	6	1	—	—	—
Prague	Czech Republic	Oct/Nov 1994	16	1	—	—	—
Rome	Italy	January 1998	59	16	—	—	—
Santiago	Chile	June 1996	117	3	1	1	1
Santiago	Chile	Nov 1996	160	4			
Shenzen	China	May 1997	—	—	1	1	1
Sofia	Bulgaria	Oct/Nov 1994	16	—	—	—	—
Taipei	Taiwan	Mar/Apr 1996	48	—	—	—	—
Vienna	Austria	Oct/Nov 1994	14	2	—	—	—
Warsaw	Poland	Oct/Nov 1994	17	—	—	—	—
Zagreb	Croatia	Oct/Nov 1994	16	—	—	—	—

stainless-steel loop immersed in liquid nitrogen. No traps were used to remove CO_2 or water from the samples. The total volume sampled was measured by pressure difference using a capacitance manometer. Once the sample was trapped, the preconcentration loop was isolated and warmed to 80°C. When the four independently programmed GCs were at their appropriate initial temperatures, they were allowed to equilibrate for exactly 20 s, then the sample was injected. The hydrogen carrier gas flushed the sample loop to the splitter which quantitatively and reproducibly split the flow in six ways to the respective columns. Flame ionization detectors (FIDs) were used with a 30 m × 0.53 mm ID Alumina PLOT column (J&W Scientific, Folsom, CA) for the light hydrocarbons (C_2–C_5), a 60 m × 0.25 mm ID, 1 μm film thickness DB-1 column (J&W Scientific, Folsom, CA) for C_3–C_{10} NMHCs, and a 60 m × 0.25 mm I.D., 0.25 μm film thickness Cyclodex-B column (J&W Scientific, Folsom, CA) for the C_6–C_{10} NMHCs. Connected to the electron capture detectors (ECDs) were a 60 m × 0.25 mm ID, 1 μm film thickness DB-1 column (J&W Scientific, Folsom, CA) for C_1–C_2 halocarbons, a 60 m × 0.25 mm ID, 0.5 μm film thickness DB-5MS column (J&W Scientific, Folsom, CA) for C_1–C_2 halocarbons and methyl nitrate, and a 60 m × 0.25 mm ID, 0.25 μm film thickness Rtx-1701 (Restex Corporation, Bellefonte, PA) column for C_1–C_2 halocarbons and C_1–C_4 alkyl nitrates. For this system configuration, 27.0% of the carrier flow was directed to the PLOT/FID, 18.9% to the DB-1/ECD, 16.2% to the DB-1/FID, 16.1% to the DB-5MS/ECD, 11.0% to the Cyclodex-B/FID, and 10.8% to the Rtx-1701/ECD.

For air sample analysis, the working standard was a pressurized whole air sample contained in an Aculife-treated Luxfer cylinder that was collected at Niwot Ridge, CO. It was assayed after every four samples in the same manner used to analyze the canister samples. The time required for one complete cycle of sample trapping, injecting, and chromatographic separation, was 20.5 min. To monitor any drift in the standard or the analytical system, four other pressurized whole air standards were also assayed at daily and weekly intervals throughout the analysis period. Mixing ratios of all quantified gases in the standards exhibited no statistically significant changes (less than 1σ) over the duration of the analysis periods. The measurement precision for the xylenes was 5% while the limit of detection was 10 pptv for the 250 ml (STP) sample size. The absolute calibration of these standards and further analytical details are described in Blake et al. (1992, 1994) and Sive (1998).

Liquid gasoline samples were diluted in *n*-pentane, then analyzed by direct injections into a Hewlett-Packard gas chromatograph equipped with a mass spectrometer (G1800A GCD) utilizing electronic impact. The apparatus was equipped with a Cyclodex B (0.25 mm I.D., 60 m, 0.25 μm film thickness) capillary column.

3. Results and discussion

3.1. Gas chromatography performances

In order to measure as many hydrocarbons as possible, many research groups rely on analyses performed using a single-gas chromatography column system, containing a very versatile stationary phase, allowing for separation of a wide range of gases typical of urban air. However, using these versatile phases (mostly DB-1 (100% dimethylpolysiloxane), or PLOT Al_2O_3 or DB-5 MS (5%-phenyl-methylpolysiloxane)), it is not possible to obtain baseline resolution for the *m*- and *p*-xylene. Thus, these gases are often reported as (*m* + *p*)-xylene (Table 2) and it is usually assumed that they are of equal concentration.

The Cyclodex-B column, which has a much different stationary phase ((14%-cyanopropylphenyl)-methylpolysiloxane blended with cyclodextrin), is primarily used to resolve chiral compounds. However, we have found that baseline resolution of the xylenes is attainable using this column. The chromatograms from a DB-1 column, DB-5MS column, and a Cyclodex-B column of a synthetic standard containing the xylenes and other NMHCs are shown in Fig. 1. This figure illustrates how differently these three columns separate the xylenes. Of these columns, only the Cyclodex-B is capable of baseline resolution for the xylenes. Furthermore, because of retention time shift, and because of coeluting unidentified and identified peaks, the quality assurance of hydrocarbon analysis is largely improved with a multidimensional column analytical system including at least one specific phase for high volatile hydrocarbons, and one specific phase for low volatile hydrocarbons. It is clear from Table 2 and Fig. 1 that such a system is necessary for the analysis of a large number of hydrocarbons (C_2–C_{10}), and in particular for *m*- and *p*-xylene speciation with good resolution in urban samples, which are heavily loaded.

3.2. Ambient air and liquid fuel analysis

As seen in Table 3, median urban mixing ratios of NMHCs vary over a wide range. Because mixing ratios are affected by the boundary layer height ratios between several NMHCs including C_6–C_8 monoaromatics have been calculated.

3.2.1. The xylenes and ethylbenzene ratios

3.2.1.1. The sum of m- and p-xylene versus ethylbenzene mixing ratios. Nelson and Quigley (1983) have shown that this ratio was constant throughout different sources such as vehicle exhaust, solvent petrol and fuel evaporation. They found a (*m*, *p*)-xylene/ethylbenzene (X/E)

Table 2
Comparison of different GC techniques to analyse hydrocarbons, halocarbons and oxy HC in ambient air: a focus on *m*- and *p*-xylene speciation

p-Xylene, *m*-Xylene speciation	Number of organic compounds speciated	GC column phase used[a]	Reference
No	18 HC[b]	BP1[c] (C_1–C_8)	Bailey et al. (1990)
No	38 HC	PLOT (C_2–C_{10})	Duffy and Nelson (1996)
No	37 HC	PLOT (C_2–C_9)	Brocco et al. (1997)
No	16 HC	PLOT (C_2–C_9)	Bruckmann et al. (1988)
No	57 HC	DB-1 (C_3–C_{10})	Moschonas and Glavas (1996)
No	33 HC	OV-101 (C_2–C_{10})	Lanzerstorfer and Puxbaum (1990)
No	16 HC + 4 oxyHC	DB 5 MS (C_3–C_8)	Goldan et al. (1995)
No	140 HC	Dual-column (in parallel): PLOT (C_1–C_9) CP-SIL 8 (C_8–C_{16})	Jemma et al. (1995)
No	16 HC	Dual-column (in series): Packed Porapak QS (C_1–C_2) WCOT ($\geqslant C_3$)	Sigsby et al. (1987)
No	53 HC	Dual-column (in parallel): SE-30[c] (C_4–C_{12}) Packed durapak (C_2–C_6)	Nelson and Quigley (1984)
Yes	50 HC	Dual-column (in series): Squalane/DB-1	Tsujino and Kuwata (1993)
Yes	5 HC (aromatics)	Ucon LB SCOT (after extraction with CS_2)	Wathne (1983)
Yes	23 HC	Dual-column (in parallel): Packed silica gel (C_2–C_3) Quadrex (125 m × 0.5 mm) (C_4–C_{13})	Zweidinger et al. (1988)
Yes	80 volatile and semi-volatile HC	Multidimensional (in parallel): PLOT (C_1–C_4) DB-Wax (C_1–C_4) HP-Ultra-1 (C_5–C_{12})	Olson et al. (1992)
Yes	46 HC	Dual-column (in series): WCOT-CP-Sil-CB (C_4–C_9) WCOT-CP-Wax-CB ($> C_9$)	Rappenglück et al. (1998)
Yes		Multidimensional (in parallel):	This study
	55 HC (FID)	PLOT (C_2–C_5) HC DB-1 (C_2–C_{10}) HC Cyclodex-B (C_6–C_{10}) HC	
	30 halocarbons and alkylnitrate (ECD)	DB-1 (C_1–C_2 halocarbons) DB-5MS (C_1–C_2 halocarbons and CH_3NO_2) Rtx-1701 (C_1–C_2 halocarbons and C_1–C_2 alkylnitrate)	

[a]Capillary columns when not specified.
[b]HC = hydrocarbons.
[c]Equivalent to DB-1 phase.

ratio of 3.6 in the Sydney area, which compared well to a few other studies. Table 4 summarizes this ratio calculated from more recent data found in the literature, and compared to our results. The X/E ratio in different source samples is relatively constant (from 2.8 to 4.6) except from the work by Siegl et al. (1999), who found a ratio of 15.5. However, these authors found extremely low emissions of xylenes and ethylbenzene, likely leading to large uncertainties. Including our values, the overall average value for the X/E ratio in different source samples is 3.5 ± 0.5. Far from local source influence, in urban and suburban areas, the X/E ratio is lower, and spreads over a larger range, especially for low values (from 1.3 to 4.5). This indicates that the xylene and ethylbenzene are emitted by the same major sources, but decay at different rates from OH-oxidation in the atmosphere. Therefore,

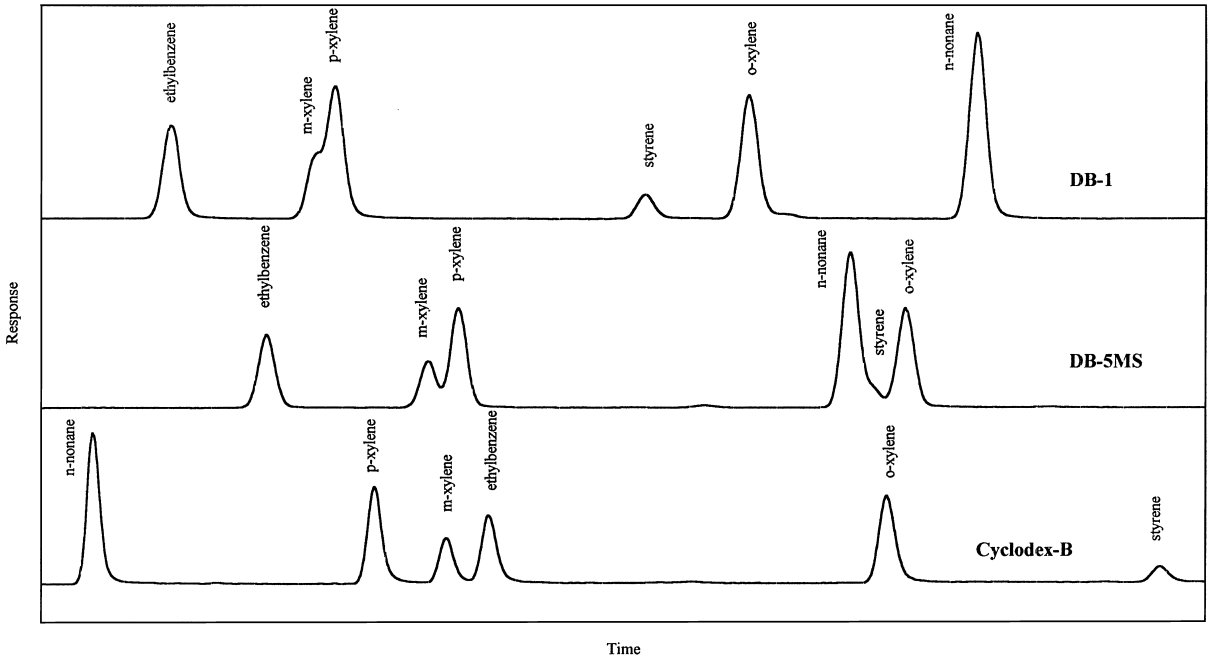


Fig. 1. Synthetic air standard chromatograms (this study).

Table 3
Urban median mixing ratios compared to traffic median mixing ratios in each city (this study)

Mixing ratios (ppbv)	Ethene	Ethyne	*n*-Pentane	Benzene	Toluene	*p*-Xylene	*m*-Xylene	*o*-Xylene	Ethylbenzene
Berlin	10.6	8.91	4.58	2.09	3.84	0.57	1.39	0.76	0.78
Berlin traffic	44.1	44.5	15.7	10.3	23.0	2.60	6.35	3.54	3.60
Bucharest	8.14	12.2	1.95	1.75	3.83	0.39	1.02	0.62	0.63
Bucharest traffic[a]	142	264	25.5	32.0	50.6	10.7	28.7	17.3	11.0
Budapest	5.11	5.33	1.19	1.28	1.96	0.34	0.82	0.42	0.40
Dresden	3.12	2.49	0.96	0.74	1.15	0.16	0.41	0.22	0.27
Krakow	7.85	9.33	1.77	2.43	2.76	0.35	0.91	0.45	0.50
Krakow traffic[a]	79.3	128	69.6	31.7	83.8	11.0	27.6	16.1	14.3
Prague	10.5	10.2	3.54	2.46	3.49	0.38	0.86	0.48	0.67
Prague traffic[a]	224	169	71.4	62.7	98.1	21.9	50.5	28.1	25.6
Sofia	11.0	18.4	4.32	3.40	5.50	1.02	2.46	1.62	1.27
Vienna	3.55	3.49	0.84	0.99	1.17	0.19	0.50	0.28	0.25
Vienna traffic (avg)	39.8	43.2	15.0	13.3	21.9	4.0	9.43	5.79	4.43
Warsaw	3.19	3.03	0.77	0.75	0.96	0.14	0.32	0.21	0.19
Zagreb	12.8	12.7	2.95	3.12	6.85	0.55	1.25	0.70	0.70
London	3.44	4.13	1.34	0.80	2.01	0.27	0.70	0.37	0.40
London traffic[a]	97.5	88.5	25.0	22.0	36.5	5.45	13.5	7.79	6.96
Paris 94	4.88	6.58	1.24	1.42	3.28	0.47	1.15	0.60	0.57
Paris 94 traffic[a]	12.1	15.6	3.09	3.98	9.47	1.25	3.04	1.69	1.62
Paris 96	2.22	1.97	0.64	0.68	2.36	0.25	0.57	0.29	0.37
Paris 98 traffic	50.2	39.9	—	34.4	65.7	7.92	18.4	9.79	8.94
Roma	7.33	9.05	1.80	3.62	9.28	1.49	3.84	2.06	1.77
Roma traffic	21.3	22.9	3.77	8.20	21.4	4.28	10.4	5.77	4.48
Santiago Nov	4.94	4.44	2.11	1.39	5.43	0.75	1.60	0.91	0.70
Santiago Nov traffic	128	68.3	23.2	17.6[a]	28.1	4.26	11.9	6.03	4.86
Santiago June	29.6	28.5	6.66	6.07	22.9	3.38	7.37	3.92	2.96
Santiago June traffic	49.7	38.4	7.69	11.8	18.3	2.91	7.00	3.39	2.78
Taipei	5.42	7.59	1.19	0.52	1.49	0.15	0.37	0.21	0.18
HongKong	2.70	3.30	0.55	1.64	4.45	0.26	0.62	0.38	0.57

[a]One sample.

Table 4
Comparison of the $(m + p)$-xylene/ethylbenzene ratios over different locations, and type of samples

Source samples	Location	X/E ratio	Reference
Exhaust: model diesel- and gasoline-fueled vehicles	US (California) fleet	2.81	Jemma et al. (1995)
Exhaust: model vehicles	UK fleet	2.98	Bailey et al. (1990)
Exhaust: model gasoline engines non-catalyst and catalyst equipped	US (Los Angeles basin) fleet	3.10	Harley et al. (1992)
Exhaust: model vehicles	US fleet	3.15	Sigsby et al. (1987)
Traffic: roadside study	US Highways	3.34	Zweidinger et al. (1988)
Exhaust: stratified-charge engine	—	3.39	Olson et al. (1992)
Traffic: tunnel study	Zürich (Switzerland)	3.39	Stahelin et al. (1998)
Exhaust: 300 model vehicles	Sydney fleet (Australia)	3.42	Nelson and Quigley (1984)
Exhaust: 67 model vehicles	Sydney fleet (Australia)	3.47	Nelson and Quigley (1983)
Traffic: tunnel study	Sydney (Australia)	3.64	Duffy and Nelson (1996)
Exhaust: model diesel-fueled vehicle	German fleet	15.5	Siegl et al. (1999)
Evaporative emissions	US fleet	3.8	Sigsby et al. (1987)
Fuels: liquid gasoline	US (Los Angeles basin) fleet	4.37	Harley et al. (1992)
Fuels: liquid and vapor	—	4.63	Olson et al. (1992)
Petrol	Sydney fleet (Australia)	4.0	Nelson and Quigley (1983)
Fuels: liquid (un)leaded gasoline	Sydney (Australia)	4.39	Duffy and Nelson (1996)
Traffic: tunnel/roadside studies	Nine worldwide different cities	3.18[a] $\pm$ 0.39	
Fuels: (un)leaded gasoline and diesel	Five worldwide different cities	3.24[a] $\pm$ 0.86	This study
Urban samples	**Location**	**X/E ratio**	**Reference**
192 samples in and over the city (Japan)	Tokyo	1.3	Wadden (1986)
Industrial area (US)	Chicago	2.70	Aronian et al. (1989)
Urban area		2.48	
Suburban background area		2	
Urban area (USA)	Boulder, Colorado	3.82	Goldan et al. (1995)
Greater urban area (Germany)	Munich	3.04	Rappenglück and Fabian (1999)
137 samples over the city (Australia)	Sydney	3.0	Nelson et al. (1983)
Urban background monitored during 1 year (Italy)	Roma	1.55	Brocco et al. (1997)
25 samples downtown area (Germany)	Hambourg	1.34	Bruckmann et al. (1988)
Downtown area (Greece)	Athens	4.48	Moschonas and Glavas (1996)
Urban area (US)	Georgia Tech campus, Atlanta	1.36	Chameides et al. (1992)
Industrial area (US)	San Jose	2.47	Singh et al. (1992)
Semi-rural site (Austria)	Vienna	2.39	Lanzerstorfer and Puxbaum (1990)
Suburban site (Greece)	Athens	2.82	
Downtown		2.46	Rappenglück et al. (1998)
Urban background sites within 11 cities (UK)	Birmingham, Cardiff , UC London, Leeds, Edinburgh, Bristol, London Eltham, Belfast, Middlesbrough, Southampton, Liverpool	2.90	Derwent et al. (2000)
Downtown and suburban sites (US)	Los Angeles bassin	3.36	Lurman and Main (1992)
Urban background sites	16 worldwide spread cities	3.03[a] $\pm$ 0.79	This study

[a]Median values $\pm 2\sigma$.

as mentioned by Nelson and Quigley (1983), the X/E ratio is a tool to investigate the photochemical age of an urban plume. However, the difference in oxidation rate between *m*-xylene and ethylbenzene is even larger, making this ratio an even better tool to determine the photo chemical age of an urban plume (see below).

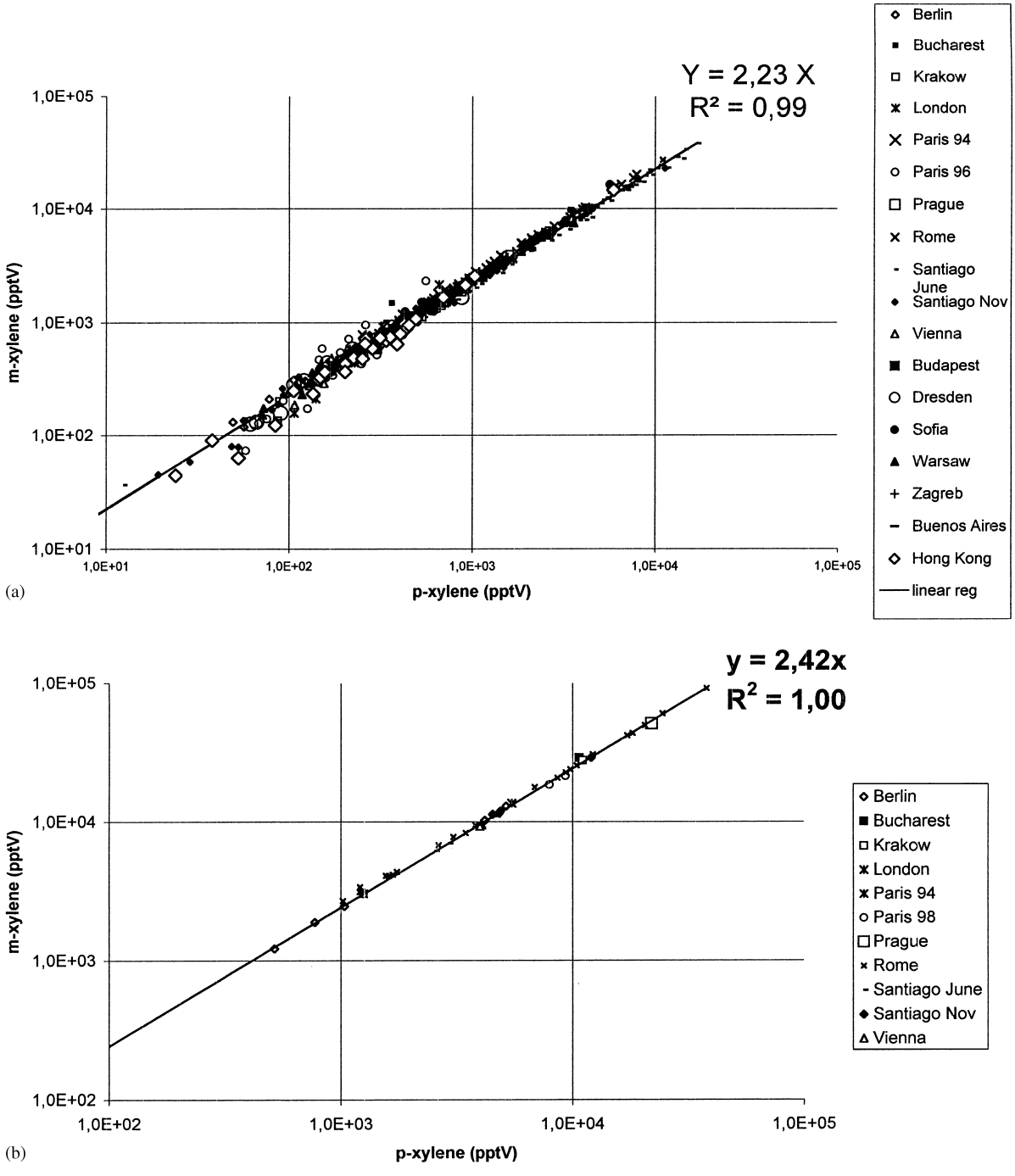
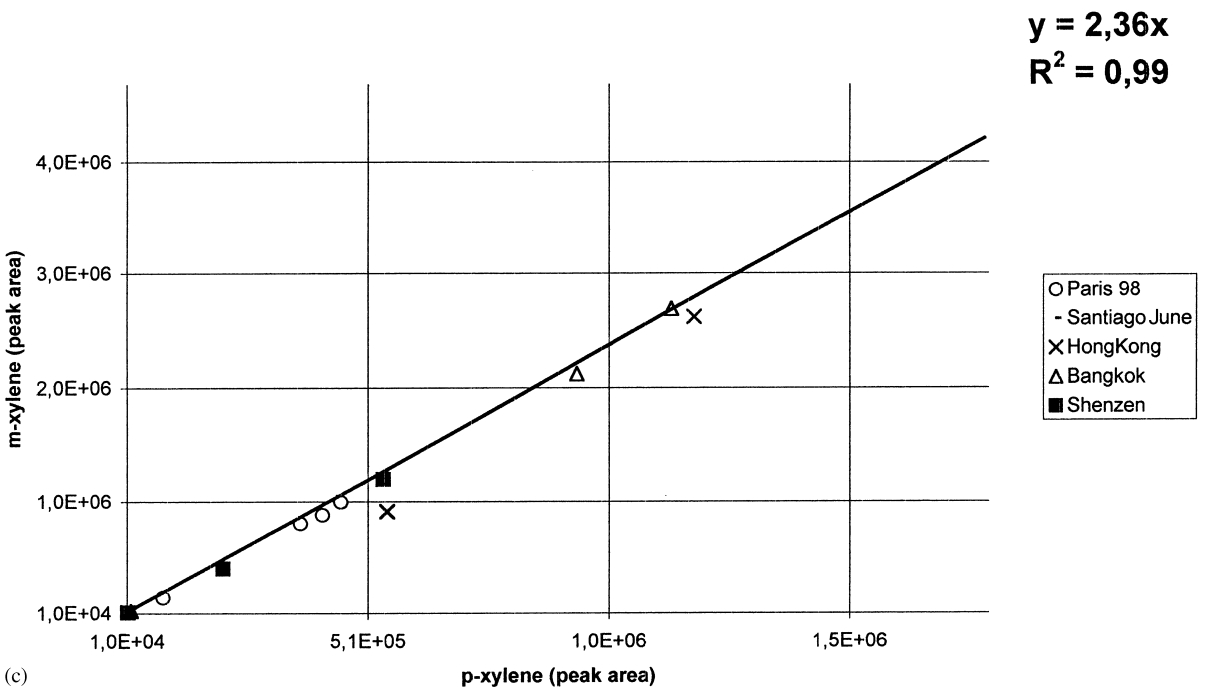
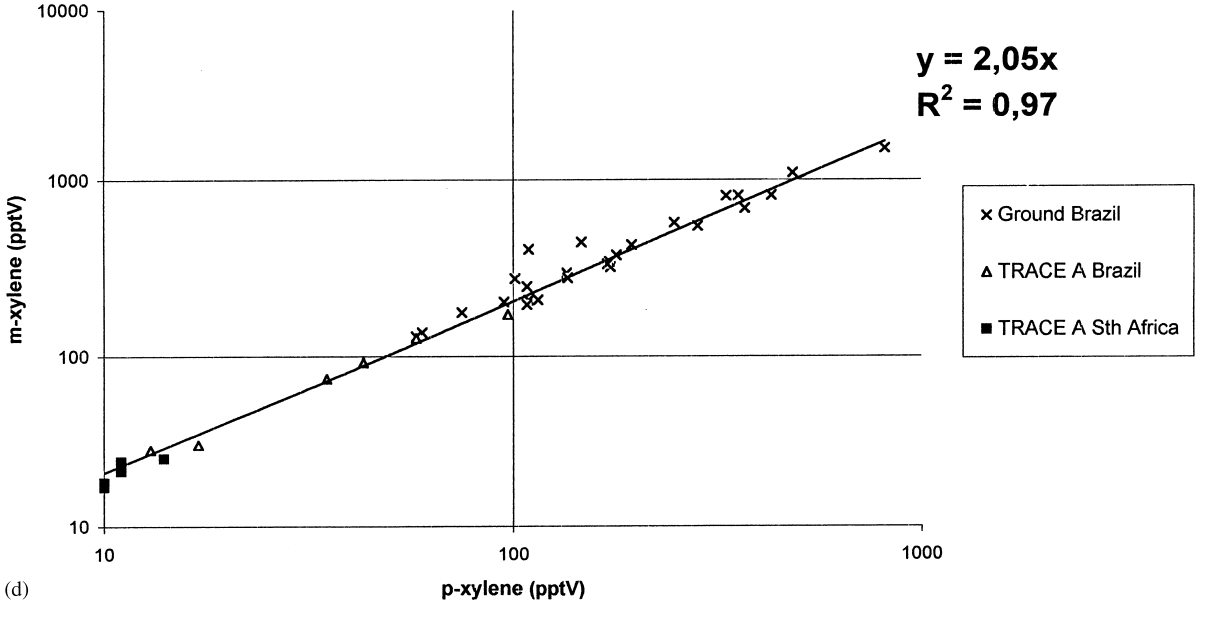


Fig. 2. (a) Urban air; (b) Traffic air; (c) Liquid fuel; (d) Biomass burning (this study).



(c)



(d)

Fig. 2. (*Continued*)

3.2.1.2. m-Xylene versus p-xylene mixing ratios

In our urban air samples, *p*- and *m*-xylene mixing ratios vary from 0.13 to 3.25 ppbv and from 0.32 to 7.05 ppbv, respectively. In each city, these mixing ratios are enhanced in traffic samples, indicating a significant vehiclar source. Although *m*- and *p*-xylene concentrations span a large range, they are exceptionally well correlated ($R^2 = 0.99$) in urban air throughout the different locations studied and during the different times of the year during the years of the study (Fig. 2a). This indicates that *p*- and *m*-xylene sources are identical throughout the different urban environments. In traffic air samples, these

Table 5
Boiling points and OH rate constant of several hydrocarbons and aromatic compounds

Compound	Boiling point (°C)[a]	k_{OH} ($\times 10^{-12}$ cm^3 molecules^{-1} s^{-1})[b]	Atmospheric lifetime[c]
m-Xylene	139.12	23.6	11.8 h
p-Xylene	138.37	14.3	19.4 h
o-Xylene	144.5	13.7	20.3 h
Ethene	− 103.7	8.52	1.3 days
Ethylbenzene	136.19	7.1	1.6 days
Toluene	110.63	6.05	1.9 days
n-Pentane	36.1	4	2.9 days
Benzene	80.09	1.21	9.4 days
Ethyne	− 84.0	0.90	13.0 days

[a]From Lide (1994–95).
[b]Rate constant towards OH radical at 298 K, from Atkinson (1994) and Semadeni et al. (1995).
[c]Assuming [OH] = 10^6 rad cm^{-3}.

compounds are also well correlated throughout the different locations (Fig. 2b), and the slope is not significantly different from the one obtained from ambient urban air samples.

The composition of fuels varies widely by city and type of gasoline (Sigsby et al., 1987; Jemma et al., 1995). However, in our data, there is a very good correlation between *m*- and *p*-xylene concentrations throughout the different fuels from the different cities studied (Fig. 2c). The slope is also in very good agreement with those obtained for both urban air and traffic air samples. Because *p*- and *m*-xylene's boiling points are very close (Table 5), the good slope agreement may indicate that in traffic air and urban air, *p*- and *m*-xylene concentrations result from fuel evaporation. However, this is only partially true because xylenes are also generated during combustion processes (Sigsby et al., 1987). Therefore, we have examined the alkylbenzene versus combustion and evaporative markers (see below).

We also compared the *m*- and *p*-xylene mixing ratios in totally different types of combustion. We considered three different biomass burning data sets where background concentrations of the xylenes were below detection limit. Airborne samples collected near fires in Brazil – 1995 (Ferek et al., 1998) and during the Transport and Atmospheric Chemistry near the Equator–Atlantic (TRACE A) project over both Brazil and Africa – 1992 (Blake et al., 1997). A good correlation between *m*- and *p*-xylene was found (Fig. 2d), with a slope not significantly different from those obtained in urban air, traffic air and fuels. The slightly lower correlation coefficient can be attributed to the much lower concentrations observed, closer to the detection limit, thus, larger measurement error bars.

To our knowledge, this is the first time that *m*- and *p*-xylene are analyzed on a large number of samples collected at various places around the world. Their relative mixing ratios remain surprisingly constant whatever the location, type of combustion and the type of fuels used: using all our 706 samples, we obtain a value of 2.33 ± 0.30 for the *m*-xylene/*p*-xylene ratio.

3.2.1.3. m-Xylene versus o-xylene mixing ratios. As with *m*- and *p*-xylene, *o*- and *m*-xylene are also well correlated, and their relative mixing ratios remain constant (within the estimated error) for urban air, traffic air, biomass combustion and fuel samples. Using all of our 706 samples (including urban and traffic air, fuel samples and fire samples), we obtain a value of 1.84 ± 0.25 for the *m*-xylene/*o*-xylene ratio.

3.2.1.4. m-Xylene versus ethylbenzene mixing ratios. *m*-Xylene and ethylbenzene are also very well correlated for heavy loaded urban, traffic, and liquid fuel samples, and the slope obtained remains constant: using all the samples taken close to the sources (all except "urban low" and "biomass burning" samples), a value of 2.24 ± 0.33 for the *m*-xylene/ethylbenzene ratio is obtained. The "urban low concentrations" data sets exhibit slope values significantly lower. Therefore, *m*-xylene and ethylbenzene are emitted by the same sources, but because *m*-xylene's atmospheric lifetime is significantly shorter than that of ethylbenzene (respectively, 11.8 h and 1.6 days; see Table 5), their relative mixing ratios decrease rapidly far from their common sources. This indicates that the *m*-xylene/ethylbenzene ratio provides a good tool to investigate the age of an urban plume.

3.3. Comparisons between C_2-alkyl benzene, toluene and benzene

3.3.1. Toluene versus ethylbenzene mixing ratios

It is clear from above that the three xylenes and ethylbenzene are emitted by the same sources in all the urban locations investigated during this study. Thus, we compared one of them, ethylbenzene, to a ubiquitous

Table 6
Correlation between the C_6, C_7 and C_8 monoaromatic compounds, and with ethene (combustion marker), and *n*-pentane (solvent evaporation marker) (in this study)

	m-Xylene/*p*-xylene		*m*-Xylene/*o*-xylene		*m*-Xylene/ethylbenzene		Toluene/ethylbenzene		Benzene/ethylbenzene		Toluene/benzene		Ethene/ethylbenzene		*n*-Pentane/Ethylbenzene	
	Slope	R^2	Slope	R^2	Slope	R^2	Slope	R^2	Slope	R^2	Slope	R^2	Slope	R^2	slope	R^2
Urban	2.23	0.99	1.91	0.99	2.37	0.98	8.27	0.77	2.58	0.77	1.93	0.66	9.74	0.70	2.74	0.55
Urban low[a]	2.32	0.95	1.74	0.91	1.62	0.70	8.99	0.12	2.79	0.48	1.94	0.05	10.4	0.10	2.97	0.12
Traffic	2.42	0.99	1.81	0.99	2.33	0.98	5.24	0.94	2.16	0.87	2.30	0.91	5.85	0.31	1.50	0.22
Fuel	2.36	0.98	1.63	0.99	2.97	0.97	3.60	− 0.50	0.97	− 0.14	1.48	0.88	—	—	—	—
Biomass burning	2.05	0.97	2.04	0.99	1.12[b]	0.98[b]	9.41[b]	0.98[b]	24.3	0.73	0.45[b]	0.95[b]	140[b]	0.92[b]	0.49[b]	0.69[b]

[a]Urban low represents the urban data for which [*m*-xylene] < 1200 pptv.
[b]Only in ground samples from Brazil 1995 (no data available in TRACE A for ethylbenzene).

aromatic compound in urban air, toluene. We chose ethylbenzene because its atmospheric lifetime towards OH radicals is comparable to that of toluene (Table 5).

Toluene versus ethylbenzene plots exhibit good correlation in traffic samples ($R^2 = 0.94$) but are poorly correlated in liquid fuel samples ($R^2 = -0.50$) (Table 6). Although toluene and ethylbenzene are known to be emitted by both fuel evaporation and combustion processes (Sigsby et al., 1987), the good correlation in traffic samples and the poor correlation in fuel samples indicate that combustion is the dominant common source for these compounds in areas dominated by automotive emissions.

Although toluene and ethylbenzene have comparable atmospheric lifetimes, the "urban air" samples exhibit a significantly poorer correlation between toluene and ethylbenzene and a higher slope value as compared to traffic samples. This may be the consequence of extra sources of toluene in cities, such as architectural surface coatings, graphic arts, industrial solvents and chemical feedstock (Aronian et al., 1989; Harley et al., 1992).

Toluene and ethylbenzene are also very well correlated in biomass combustion samples (Table 6), but the slope is significantly higher than in traffic air samples.

3.3.2. Benzene versus ethylbenzene mixing ratios

Benzene is also a ubiquitous compound in urban air, and there is a strong desire to reduce its emissions because it is carcinogenic. The correlation between ethylbenzene and benzene lead to the same conclusions as for toluene versus ethylbenzene except that the correlation coefficients are lower, in part because their atmospheric lifetimes towards OH radicals are different (Table 5).

3.3.3. Toluene versus benzene mixing ratios

Toluene and benzene are well correlated throughout traffic, biomass burning and fuel samples, while the slopes vary widely: toluene is more concentrated in all the city samples, whereas benzene is dominant in biomass burning samples. The correlation is poorer in "urban air" samples, likely because of extra sources other than combustion, and also because of the difference in their atmospheric lifetimes towards OH radicals.

3.3.4. Influence of catalytic converters

It has been previously shown that concentrations correlation between benzene and toluene and between benzene and C_2-alkylbenzenes are very good in car exhaust without catalytic converters whereas they are poor in car exhaust equipped with catalytic converters (Heeb et al., 1999). One measure of catalytic converter efficiency is the ethene/ethyne ratio: it is 3 or above for well maintained catalyst-equipped vehicles whereas it is closer to 1 for non-catalyst vehicles (Hoekman, 1992; Duffy and Nelson, 1996). In our samples, the ethene/ethyne ratio is closer to 1 than to 3 in all the locations investigated. This

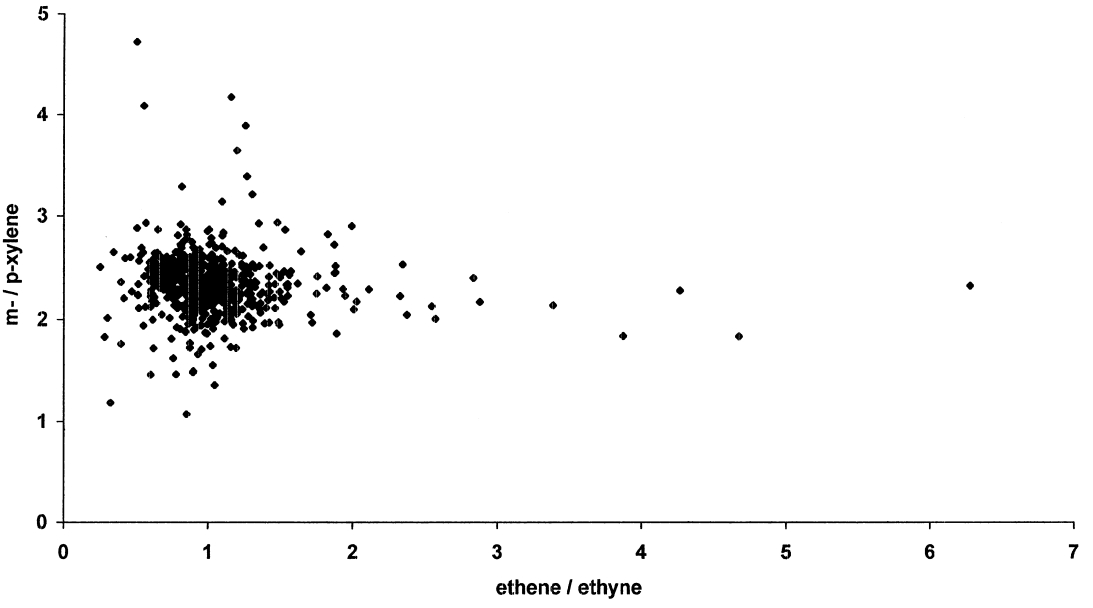


Fig. 3. Influence of catalytic converters markers on *m*-/*p*-xylene ratios (this study).

suggests that the proportion of active catalytic converters was small or that the majority of emissions came from non-catalyst equipped vehicles. Therefore, the good correlations observed in traffic samples between toluene and ethylbenzene, between benzene and ethylbenzene and between toluene and benzene are in good agreement with the study by Heeb et al. (1999). However, C_2-alkylbenzenes ratios should not be significantly affected by the quantity of active catalytic converters. The reason for this is that only benzene/alkylbenzenes ratios are significantly affected by active catalytic converter use because it is likely that alkylbenzenes are dealkylated (to form benzene) by the converters (Hoekman, 1992; Duffy and Nelson, 1996; Heeb et al., 1999). Furthermore, although a relatively significant evolution is observed in ethene/ethyne ratios in Paris (1994, 1996 and 1998), the corresponding *m*-xylene/*p*-xylene ratios remain statistically constant. Finally, one can see from Fig. 3 that the ethene/ethyne ratio does not significantly influence the *m*-xylene/*p*-xylene ratio, indicating that the use of catalytic converters does not influence the *m*-xylene/*p*-xylene ratio which remains statistically constant.

3.4. Comparisons between the C_2-alkylbenzenes and source emission markers

It is obvious from above that the C_2-alkylbenzenes are emitted by the same sources. To distinguish between combustion and solvent evaporation sources, two comparisons have been made: one between the C_2-alkylbenzenes and ethene, which is a marker for combustion, and one between the C_2-alkylbenzenes and *n*-pentane which is a marker for solvent evaporation (even if this component is also emitted in combustion processes). Ethylbenzene has been chosen representative of the C_2-alkylbenzenes because its atmospheric lifetime towards OH-oxidation is comparable to that of ethene and *n*-pentane (Table 5). The comparisons between ethene and ethylbenzene and between *n*-pentane and ethylbenzene show a very low correlation throughout all the cities investigated (Table 6). The correlation coefficients are particularly low in traffic samples ($R^2 = 0.31$ and 0.22, respectively). Investigating each city individually, one finds good correlation between ethylbenzene and ethene and between ethylbenzene and *n*-pentane, with slopes varying widely (from 0.035 to 0.26, and from 0.13 to 0.98, respectively). This explains the poor correlation found when all locations were grouped together. In most cities, "urban air" samples show both ethylbenzene/ethene and ethylbenzene/*n*-pentane ratios consistent with those in the traffic samples (Table 7). This indicates that the unique urban source for C_2-alkylbenzenes is automotive emissions, and the comparisons between toluene and ethylbenzene indicates that combustion may be the major source for these compounds (see above). However, this does not apply for three cities: Santiago (November), Krakow, and Prague.

In Santiago (November), the ratio between ethylbenzene and ethene is significantly higher in "urban air" samples than in traffic samples, indicating that extra sources (other than automotive) of ethylbenzene exist in the urban area. Because the ratio between ethylbenzene and *n*-pentane is statistically the same in "urban air" samples and in traffic samples, the extra sources may be solvent evaporation from factories, or chemical feedstock.

Table 7
Comparison between one C_2 alkylbenzene and (i) one combustion marker (ethene) and (ii) one evaporation marker (*n*-pentane) for each city in urban air and traffic air in this study

	Ethylbenzene/ethene				
Urban air	Ethylbenzene/ethene		Traffic air	Ethylbenzene/ethene	
	Ratio	$\pm 2\sigma$		Ratio	$\pm 2\sigma$
Roma	0.21	0.07	Roma	0.26	0.08
Paris 96	0.14	0.08	Paris 98	0.15	0.04
Paris 94	0.13	0.01	Paris 94	0.13	—
Berlin	0.072	0.022	Berlin	0.075	0.016
Santiago Nv	0.073	0.046	Santiago Nv	0.040	0.003
Santiago Jn	0.070	0.091	Santiago Jn	0.068	0.041
Bucharest	0.073	0.032	Bucharest	0.077	—
Budapest	0.075	0.021	—	—	—
Dresden	0.064	0.036	—	—	—
Krakow	0.066	0.024	Krakow	0.18	—
Prague	0.065	0.012	Prague	0.11	—
Sofia	0.098	0.030	—	—	—
Vienna	0.083	0.050	Vienna	0.12	0.03
Warsaw	0.053	0.020	—	—	—
Zagreb	0.059	0.012	—	—	—
London	0.10	0.03	London	0.071	—
Taipei	0.035	0.011	—	—	—
Hong Kong	0.20	0.11	—	—	—
	Ethylbenzene/ethene				
Urban air	Ethylbenzene/*n*-pentane		Traffic air	Ethylbenzene/*n*-pentane	
Roma	0.98	0.21	Roma	1.1	0.2
Paris 96	0.55	0.21	—	—	—
Paris 94	0.43	0.08	Paris 94	0.52	—
Berlin	0.18	0.01	Berlin	0.20	0.05
Santiago Nv	0.34	0.16	Santiago Nv	0.22	0.05
Santiago Jn	0.18	0.17	Santiago Jn	0.38	0.11
Bucharest	0.29	0.31	Bucharest	0.43	—
Budapest	0.30	0.05	—	—	—
Dresden	0.25	0.09	—	—	—
Krakow	0.24	0.07	Krakow	0.21	—
Prague	0.41[a]	0.81[a]	Prague	0.18	—
Sofia	0.28	0.05	—	—	—
Vienna	0.33	0.15	Vienna	0.31	0.10
Warsaw	0.25	0.08	—	—	—
Zagreb	0.19	0.08	—	—	—
London	0.30	0.09	London	0.28	—
Taipei	0.13	0.04	—	—	—
Hongkong	0.86	0.42	—	—	—

[a]Best correlation was: [ethylbenzene] $= 0.13 \times$ [*n*-pentane] $+ 238$ (in pptV), with $R^2 = 0.82$.

In Krakow, the ratio between ethylbenzene and ethene is significantly lower in "urban air" samples than in traffic samples, however, only one traffic sample was collected in this city, and the mixing ratios may not represent the mean values for automotive emissions in Krakow.

In Prague, as in Krakow, only one traffic sample was collected. However, an unknown source of ethylbenzene was determined. In "urban air" samples the actual ethylbenzene versus *n*-pentane correlation is: [ethylbenzene] $= 0.13$[*n*-pentane] $+ 238$ (pptV), with $R^2 = 0.82$. Other good correlation ($R^2 > 0.80$) with a Y intercept significantly different from zero was also observed in Prague for ethene versus *n*-pentane, *o*-xylene versus *n*-pentane, *m*-xylene versus *n*-pentane, *p*-xylene versus *n*-pentane, benzene versus *n*-pentane, toluene versus

n-pentane, *n*-butane versus *n*-pentane, *i*-butane versus *n*-pentane, ethyne versus *n*-pentane and propene versus *n*-pentane. Therefore, there is an unknown source containing ehtylbenzene, *o*-, *m*-, *p*-xylene, benzene, toluene, *n*-butane, *i*-butane, ethene, ethyne, propene but no *n*-pentane (nor *i*-pentane), but further studies need to be done in this city to identify this source.

4. Conclusions and implications for atmospheric chemistry

The persistent ratios obtained between *m*-, *p*-, *o*-xylene and ethylbenzene concentrations in all the locations investigated indicate that these compounds have the same sources everywhere in the world. Comparing them to ethene (which is a combustion marker) and to *n*-pentane (which is a solvent evaporation marker) show that in all cities except in Santiago and Prague, C_2 alkylbenzenes are emitted only by automotive sources. In Santiago, extra C_2 alkylbenzene emissions may come from solvent evaporation from factories or chemical feedstock, and in Prague, there is an unknown source containing ehtylbenzene, *o*-, *m*-, *p*-xylene, benzene, toluene, *n*-butane, *i*-butane, ethene, ethyne, propene but no *n*-pentane (nor *i*-pentane), but further studies need to be done in this city to identify this source. Comparing C_2 alkylbenzenes to toluene and benzene indicate that combustion (and not fuel evaporation) is the major common source of these compounds in areas dominated by automotive emissions. The xylenes and ethylbenzene ratios remain persistent close to their urban sources no matter of the type of combustion, of the type of fuel used, etc. Moreover, the three xylenes ratios remain similar in very different kinds of environments: urban and close to biomass combustion.

This information should be very useful for ambient air measurement networks that routinely measure the sum of the three xylenes as well as for modeling studies. These persistent ratios should also be useful in analytical testing of gas chromatography or any other aromatic hydrocarbons' analytical device and for the use of previous data sets in which *p*- and *m*-xylenes were reported as one.

Finally, the constancy of the sources of ethylbenzene and *m*-xylene and the difference in atmospheric lifetimes with respect to OH removal could be a useful tool to estimate the amount of photochemical processing in an advecting urban plume.

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